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⑥ ADDITION AND SUBSTITUTION PRODUCTS OF OXYGEN FLUORIDES

⑩ by A. G. STRENG, A. D. KIRSHENBAUM AND A. V. GROSSE

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INTRODUCTION

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This is the Third Annual Progress ~~Report for~~ the Office of Naval Research, Contract Nonr 3085(01). It covers the period from Jan~~uary~~ 1 ~~to~~ - Dec~~ember~~ 31, ~~1~~962.

The research program was specified by the Research and Development Task Order and consists of the two following subjects:

I. The synthesis and characterization of the oxygen fluorides.

II. The synthesis and characterization of certain substitution and addition products of the oxygen fluorides.

SUMMARY

Chemical reactions of oxygen fluorides were studied to obtain addition products of high oxidizing power. The chemical characterization of dioxygen difluoride is given, and the reactions of formation of the intermediate compounds O_2ClF_3, O_2BrF_5 and O_2SF_6, as well as some others, are described.

A new method ~~(namely by~~ (electric discharge) of preparing xenon tetrafluoride, XeF_4, is given. The preparation of xenon oxyfluorides is indicated.

Using the same method, at liquid air temperatures, it was possible to synthesize the first compound of krypton, i.e., krypton tetrafluoride or KrF_4[7]. It forms beautiful colorless transparent crystals, more volatile and less thermally stable than XeF_4[7].

I. REACTION OF O_2F_2 WITH PLATINUM FLUORIDES

The starting point of our investigation was an attempt to prepare the interesting and new oxygen compound:

$$O_2^+ [PtF_6]^- ,$$

discovered by Neil Bartlett(1) of the University of British Columbia in Vancouver. It was this compound that led him to isolate the first typical chemical compound of xenon(2) or

$$Xe^+ [PtF_6]^-$$

The O_2PtF_6 compound was synthesized directly by mixing O_2-gas with an equimolar quantity of PtF_6 at 21°C., in line with the equation:

$$O_2 + PtF_6 \rightarrow O_2 PtF_6. \qquad (1)$$

The compound is a deep red solid, which sublimes to a bromine-colored vapor at about 155°C. It melts under pressure at 200°C. It has a cubic unit cell with $a = 10.032 \pm 0.002$ Å, with 8 molecules/cell, and probably belongs to the space group T_h^7 - Ia3. Its density (X-ray) = 4.48 g/cm^3. Its magnetic moment, $\mu_{eff.} = 2.46$ Bohr magnetons @ 20° and is compatible with two unpaired electrons, one due to an O_2^+ ion, the other with the d^5 system of an octahedral hexafluoroplatinate (V) ion. This compound or dioxygenyl hexafluoroplatinate (V) may also be formulated as

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(1) N. Bartlett, Proc. Chem. Soc., 1962, 115; see also l.c. 1960, 14.
(2) N. Bartlett, Proc. Chem. Soc., 1962, 218.

$$O_2^+F^-, PtF_5$$

or as an addition compound of O_2F to PtF_5. In view of our study of the oxygen fluorides, it was of interest whether the compound would form from a lower platinum fluoride and O_2F_2, for example:

$$PtF_4 + O_2F_2 \rightarrow O_2^+ [PtF_6]^- \qquad (2)$$

At present four platinum fluorides are known, as shown in Table I.

TABLE I

Discoverer		Description	M.P. °C.	B.P. °C.
PtF_2	Henry Moissan(3)	Yellow green powder, insoluble in H_2O	----	----
PtF_4	Henry Moissan(3)	Small yellow "chamois" crystals, very hygroscopic	≃400	----
PtF_5	N. Bartlett(4)	Dark red solid	75-76	300-305
PtF_6	B. Weinstock(5)	Dark red to black	56.7	v.p.=29mm.@0°C. =96mm.@21°C.

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(3) Henry Moissan's "De Fluor", 1900, p. 216-222.
(4) N. Bartlett, D. H. Hofmann, Proc. Chem. Soc., 1960, 14-15.
(5) B. Weinstock, H. H. Claassen and J. G. Malm, J. Am. Chem. Soc., 79, 5832 (1957).

In our experiments, Pt-sheet and ribbon were heated in a Pt-boat placed in a Ni-tube, to 500°C. and fluorinated with elementary dry HF-free fluorine to a mixture of PtF_4, PtF_5, with probably some PtF_6. To about 10 g. of Pt-fluoride in an evacuated Pyrex test tube 2.00 cc. of liquid O_2F_2 (m.p. 119°K.) were added, by distillation at 90°K. No reaction was observed for 15-20 minutes at 130°K. It was gradually warmed to 160°K. After 3-5 minutes at this temperature, a violent explosion took place. Under the same conditions, pure O_2F_2 does not explode or detonate, even if initiated with powerful detonators. Our experiment would indicate that the Pt-fluorides either effectively catalyze the decomposition of O_2F_2 into $O_2 + F_2$ or partly dissolve and react with O_2F_2 with heat liberation, which auto accelerates the reaction to an explosion. Obviously additional experiments, using small quantities of Pt-fluorides, preferably in a suitable solvent, are necessary to establish whether O_2PtF_6 can be formed from O_2F_2.

II. REACTION OF OXYGEN DIFLUORIDE WITH XENON

Bartlett's formulation of his new compound

$$O_2^+[PtF_6]^-$$

led him to discover⁽²⁾ the fascinating and unusual:

$$Xe^+[PtF_6]^- \quad ,$$

the first typical chemical compound of an inert gas, a feat which ran counter to the accepted theory of a "satisfied octet of valence electrons". He was led to his new compound by the simple logic that since the first ionization potential of the O_2 molecule = 12.5 ev. and that of xenon = 12.13 ev., the latter should add PtF_6 more readily than oxygen does. He found, indeed, that Xe adds to PtF_6 and forms $Xe^+[PtF_6]^-$. It is an orange-yellow solid, stable at room temperature, insoluble in CCl_4 and which can be sublimed in a vacuum. Stimulated by this discovery, Claassen, Malm and Selig(6) found that Xe and fluorine react directly at 400°C. to form the first binary compound of Xe, namely the tetrafluoride XeF_4.

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(6) Claassen, H. H., Selig, H. and Malm, J. G., J. Am. Chem. Soc., 84, 3593 (1962).

A. In a Heated Ni-Tube

Stimulated by the research originated by Bartlett and Claassen, we decided to investigate the behavior of oxygen fluorides with xenon (and also 1/2 $O_2 + F_2$ and pure O_2). A Ni-tube (2.5 cm. in diameter, vol. = 75 cm^3), closed at one end and with a valve at the other was filled with a known volume of Xe and OF_2 in a molar ratio of 1:1 and heated to a constant temperature. After reaction the tube was cooled, noncondensed gases pumped out and analyzed. Three experiments were made as follows:

EXP. 1: 312 mg. Xe and 129.5 mg. OF_2 were heated to 410°C. for 2-3/4 hours; initial pressure in tube = 3.25 atm.

After the run no unreacted OF_2 was detected; 81.0 mg. Xe and 10.5 mg. F_2 and 29.4 mg. O_2 were found in the reaction product. 320.6 mg. of colorless crystals were sublimed out of the tube. Material balance checked well (before reaction = 442 mg.; after reaction = 441 mg.). The crystals must have contained by difference (38.4 mg. O in O_2 - 29.4 mg. O_2=) 9.0 mg. O or 2.80 wt.%; thus, 23% of the O used (in the OF_2) reacted.

EXP. 2: 323.5 mg. Xe and 135.2 mg. OF_2 were heated to 400 ± 10°C. for 3.0 hours; initial pressure in tube = 3.38 atm.

After the run 65.0 mg. Xe, 9.9 mg. F_2 and 24.3 mg. O_2 (and no noticeable amounts of OF_2) were found; 361.9 mg. of colorless crystals were sublimed out of the tube. Material balance again checked well (before reaction = 458 mg.; after reaction = 461 mg.). Again by difference 15.5 mg. O should be in the crystals or 4.28 wt.% O; of the original O in OF_2, 39% reacted.

EXP. 3: Carried out first at 200°C. for 2.0 hours with no noticeable reaction and then at 300°C.

220 mg. Xe and 90 mg. OF_2 were heated to 300°C. for 4-3/4 hours. After the reaction 73 mg. Xe, 9.4 mg. O_2 and a trace of F_2 were found besides 225 mg. colorless crystals. Material balance, as follows: before reaction = 310 mg.; after reaction = 308 mg. O-content in crystals, by difference = 19.5 ~~17.2~~ mg. or 8.57 ~~5.39~~ wt.% O; thus, in EXP. 3, 54% of the oxygen of the OF_2 is contained in the crystals. Their empirical formula is:

$$Xe_{1.00}\,O_{1.1}\,F_{3.0}$$

Thus, xenon oxyfluorides containing from $\simeq$ 2.8 to 8.6 wt.% O or up to 1 atom oxygen per atom Xe are formed from OF_2 and xenon by simply heating to 400°C., as in the XeF_4 preparation. In order to see whether a mixture of 1/2 $O_2 + F_2$ would react as OF_2, an experiment was made using a mixture in the molar ratio of:

$$Xe + 1/2\ O_2 + F_2$$

In the same Ni-tube 320.5 mg. Xe, 39.0 mg. O_2 and 93.0 mg. F_2 were heated to 400°C. for 3.0 hours. Recovered were 53.8 mg. Xe, 32.1 mg. O_2 and 18.1 mg. F_2, besides 351.2 mg. of colorless crystals of xenon oxyfluorides. The material balance was good (before reaction, 453 mg.; after reaction, 455 mg.). The O-content of the crystals was by difference only 6.9 mg. or 1.97 wt.%; 18% of the original oxygen reacted.

The conclusion is that mixtures of O_2 and F_2 can be substituted for OF_2, but the oxygen content of the xenon oxyfluorides, at least from this one experiment, are less than when using OF_2.

In view of the ready formation of xenon-oxygen bonds an experiment was made with a mixture of Xe and pure O_2, in the ratio:

$$Xe + O_2$$

It was heated to 500°C. for 3.0 hours, but no noticeable formation of any reaction product could be observed. This is not to say that F-free Xe-oxides might not be prepared by other methods. Addition of small amounts of F_2, i.e., 0.1 mole per 1.0 mole O_2, to the above mixture produces small amounts of fluorides or oxyfluorides, corresponding to the fluorine content. In one run at 510°C. for 3.0 hours such a mixture of 310.0 mg. Xe, 78.6 mg. O_2 and 10.0 mg. F_2 produced only 12.3 mg. of crystals, while 300.2 mg. Xe and 70.5 mg. O_2 and no F_2 were recovered. In view of the small amounts of crystals, there was some loss estimated at $\simeq$ 16 mg. oxyfluorides.

B. In an Electric Discharge

The electric discharge apparatus used for reaction of OF_2 with Xe was similar to the one described in the Second Annual Progress Report.(7)

Xe + OF_2, 1:1 by volume mixture was admitted to the electric discharge vessel cooled to 195°K. in a dry ice + Freon 12 bath with an average velocity of about 130 cm^3/hr. (at N.T.P.).

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(7) A. G. Streng and A. V. Grosse, "Addition and Substitution Compounds of Oxygen Fluorides", Second Annual Progress Report for the Office of Naval Research, Contract Nonr 3085(01). Research Institute of Temple University, Philadelphia, Pa., January 19, 1962.

The pressure maintained in the reaction vessel was 3-62 mm. Hg; the discharge current varied from 12-32 milliampers and the voltage from 1200-3600 volts. Two runs were made. In both, transparent colorless crystals were formed.

In one case 770.7 mg. xenon and 317.0 mg. OF_2 were converted to 664.3 mg. of transparent crystals, = 61 wt.% of the Xe-OF_2 mixture, with some unreacted gas. No O_2F_2 formation was observed. Even making the improbable assumption that all of the original F-content of the OF_2 reacted to XeF_4 only, the maximum weight of XeF_4 would be 609 mg. Thus, the difference, i.e., 664-609 mg. or 55 mg. of oxygen should be present in the product. It should be a xenon oxyfluoride or a mixture of oxyfluorides.

The xenon oxyfluorides form colorless transparent crystals, stable at room temperature. They can be readily resublimed and grown to large single crystals about 2 mm. in length.

The product is being analyzed.

A picture of the crystals are shown in Figure 1.

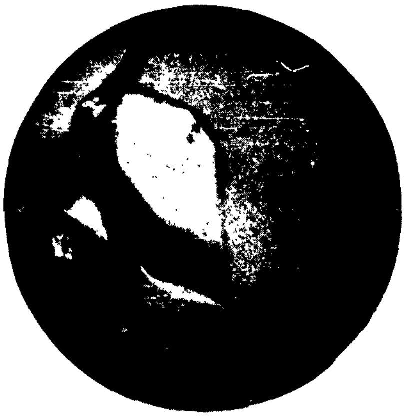

FIGURE 1. XENON OXYFLUORIDE CRYSTALS. Linear Magnification ≃ 10 x.

III. USE OF AN ELECTRIC DISCHARGE FOR PREPARATION OF XeF_4 AND KrF_4

A. Preparation of XeF_4 (8)

Thirty years ago Yost and Kaye(9) attempted to prepare fluorides of xenon by electric discharge without success. These authors stressed, however, that, "It does not follow that xenon fluoride is incapable of existing." Now that XeF_4 has been discovered by Claassen, et al.,(6,10) we have successfully prepared XeF_4 by electric discharge.

The apparatus used was very similar to the one used in our discharge preparation of O_3F_2.(11) The diameter of the reaction vessel was 6.5 cm.; the electrodes (2 cm. in diameter) were 7.5 cm. apart. A gas mixture of 1 volume Xe + 2 volumes F_2 was fed at a rate of 136 cc. per hour at N.T.P. into the reaction vessel, cooled in a 195°K. (-78°C.) dry ice-Freon 12 bath, and quantitatively converted to XeF_4. The discharge varied from 1100 volts and 31 milliamps. to 2800 volts and 12 milliamps. while the total pressure varied from 2 to 15 mm. Hg.

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(8) A. D. Kirshenbaum, A. G. Streng, L. V. Streng and A. V. Grosse, "Preparation of XeF_4 by Electric Discharge", accepted for publication in J. Am. Chem. Soc., 85 (1963).

(9) D. M. Yost and A. L. Kaye, J. Am. Chem. Soc., 55, 3890 (1933).

(10) C. L. Chernick, H. H. Claassen, et al., Science, 138, 136 (1962).

(11) A. D. Kirshenbaum and A. V. Grosse, J. Am. Chem. Soc., 81, 1277 (1959); see Fig. 1, p. 1278.

In a typical run of 3.5 hours, 7.10 mmoles. of Xe and 14.20 mmoles. of F_2 were used and 1.465 grams (7.07 mmoles.) of xenon fluoride were produced. The composition of the product, as determined from synthesis, is therefore XeF_4. The advantage of this method over Claassen's(6) thermal method is that it is continuous, quantitative and that an excess of fluorine is not required.

The composition of our products was also confirmed by analysis. A 102.3 mg. sample of XeF_4 was hydrolyzed with dilute KOH solution(6) liberating 64.9 ± 1.0% by weight of Xe (theoretical = 63.3 wt.%). The resulting solution contained, by titration with $Th(NO_3)_4$, 35.1 ± 1.0% by weight F^- (theoretical = 36.7 wt.%). In addition, a new analytical method for Xe was used. XeF_4 reacts quantitatively with excess Hg, as follows:

$$XeF_4 + 4\ Hg \rightarrow Xe \uparrow + 2\ Hg_2F_2 \quad (\text{or } 2\ HgF_2) \qquad (3)$$

A sample of 136.4 mg. of our XeF_4 gave 87.3 (± 0.5) mg. Xe or 64.0 (± 0.5) wt.%.

The product was vacuum sublimed into a glass tube and any trace of SiF_4 or O_2 pumped off; the clear colorless crystals formed were identical in appearance to those described previously.(6)

B. Preparation of KrF_4

After the preparation of XeF_4 by discharge, we succeeded in the last days of December 1962 to prepare krypton tetrafluoride, KrF_4. A molar mixture of Kr + 2 F_2 combined quantitatively to KrF_4.

It was first found that gaseous krypton and fluorine did not form noticeable amounts of krypton fluorides by heating them to 400°C. in a nickel vessel. However, by taking advantage of the Institute's experience in the preparation of the thermally very unstable O_3F_2, O_4F_2 and the violet O_2ClF_3, we were able to produce krypton fluoride. Recently, we have shown that xenon tetrafluoride can be produced quantitatively by electric discharge. Using exactly the same method, we have now been successful in producing krypton fluoride. Actually, a mixture of 1 volume krypton and 2 volumes fluorine were admitted into an electric discharge tube at 85-86°K. and at about 10 mm. total pressure. The conversion to a white solid compound, depositing on the walls of the discharge tube, was practically quantitative. In a typical experiment, 502 cc. at N.T.P. of the above mixture was quantitatively converted into krypton fluoride; 1.15 grams of krypton fluoride was produced (in 4.0 hours), which has the composition KrF_4 by

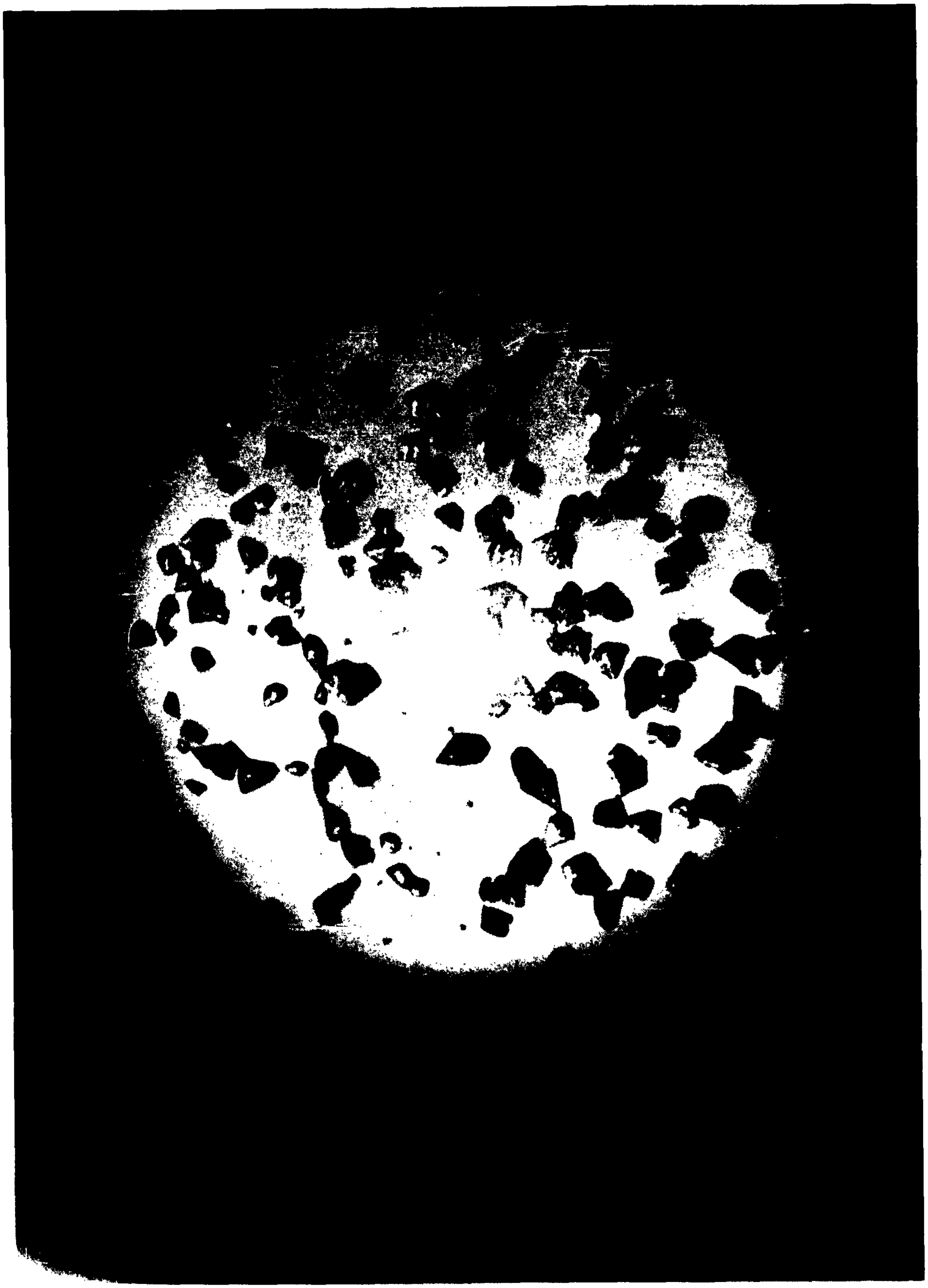

FIGURE 2. KRYPTON TETRAFLUORIDE. Linear Magnification ≃ 100 x.

synthesis. The compound is stable for at least many days and has no noticeable vapor or decomposition pressure at -78°C. The absence of any free or adsorbed krypton and fluorine is obvious from the fact that at -78°C. the vapor pressure of krypton and fluorine is above one atmosphere. Any traces of silicon tetrafluoride and free oxygen, which could be presented as impurities, (from the reaction with glass) were also absent in view of the fact that our compound had no noticeable vapor pressure at -78°C. It could be slowly sublimed at -40 to -30°C. into a liquid nitrogen trap in a vacuum. The compound forms colorless, transparent, beautiful crystals similar to xenon tetrafluoride; they are shown in Fig. 2 under a linear magnification $\simeq$ 100 x.

The vapor pressure of krypton fluoride is greater than the XeF_4 and its thermal stability is less.

IV. FORMATION AND PROPERTIES OF DIOXYGEN CHLORINE TRIFLUORIDE, $(O_2ClF_3)_n$

Dioxygen difluoride, O_2F_2, reacts with Cl_2, ClF and HCl and at certain conditions does form a deep violet addition product, $(O_2ClF_3)_n$.(7,12) The formation of this product and

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(12) A. G. Streng and A. V. Grosse, "Addition and Substitution Products of Oxygen Fluorides", First Annual Report for Office of Naval Research, Contract Nonr 3085(01). Research Institute of Temple University, Philadelphia, Pa., January 3, 1961.

its properties was studied further and the summary of results obtained is presented here.(13)

The colored polyoxygen difluorides—O_2F_2, O_3F_2 and O_4F_2(7,12)—represent the most potent oxidizers known, since they are endothermic compounds of oxygen and fluorine.

O_3F_2 decomposes into O_2F_2 and O_2 at $\simeq 120^{\circ}K.$; O_4F_2 into O_3F_2 and O_2 at about $100^{\circ}K$. In the decomposition reaction, regardless whether it proceeds with the formation of free O-F radicals or atomic oxygen, highly reactive species are formed. For this reason the addition of only 0.1 weight % O_3F_2 to liquid O_2 makes the mixture hypergolic with a wide variety of fuels, including H_2, at low temperatures.

Higher members of this series, such as O_5F_2 and O_6F_2, may exist and thus the abstraction of fluorine from the lower members by means of a suitable reaction is of particular interest. The view has been expressed(12) that in such an abstraction reaction cyclic polymers of oxygen—i.e., O_5 and O_6—may form, since the strengths of O-O and O-F bonds are similar. The red color of the polyoxygen fluorides is due to the O-O bonds, since the O-F bond in OF_2 does not give rise to any significant absorption in the visible spectrum. In this respect the colored

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(13) A. G. Streng and A. V. Grosse, Advances in Chemistry Series 36, 159 (1962).

O-O bonds in the fluorides are different from the O-O bonds in the colorless H_2O_2, or H_2O_4 and alkyl peroxides.

In our studies attempting fluorine abstraction, O_2F_2 was reacted with ClF. If the reaction is carried out without special precautions, the two substances readily react following the stoichiometric equation:

$$O_2F_2 + ClF \rightarrow O_2 + ClF_3 \qquad (3)$$

with $\Delta H_{298} = -30.1$ Kcal. per mole.

However, if the reaction is carried out under mild conditions, from just above the melting point of ClF (119°K.) up to 130°K., an intense violet colored intermediate compound of the elementary composition $(O_2ClF_3)_n$ (referred to simply as O_2ClF_3) is formed, in line with the scheme:

$$O_2F_2 + ClF \rightarrow O_2ClF_3 \qquad (4)$$

Its color and hue are very similar to those of the organic dye methyl violet.

At the beginning it was thought that the intense violet color may be due to the formation of blue ozone mixed with some unreacted red-orange O_2F_2,:

$$3\ O_2F_2 + 3\ ClF \rightarrow 2\ O_3 + 3\ ClF_3 \qquad (5)$$

It could be readily shown that no ozone formed, since the latter can be easily vacuum-distilled out of such a mixture.

The O_2ClF_3 was obtained in a purity of 81%, the other 19% being the nearly colorless ClF_3. O_2ClF_3 is a solid, thermally stable up to $195^{o}K$. At this temperature it can be kept for over a year. It has a vapor pressure of less than 12 microns at $158^{o}K.$; at this pressure and temperature it dissociates into its components, which can be collected on a liquid nitrogen finger ($77^{o}K.$). If the finger is warmed up to 119° to $140^{o}K.$, the violet compound forms again.

The compound is insoluble in liquid O_2 and O_3 at $90^{o}K.$, in liquid ClO_3F and C_3F_8 at $\simeq 140^{o}K.$, and in liquid NF_3, CCl_2F_2, and $CClF_3$ at $\simeq 160^{o}K$. It is soluble in ClF at $125^{o}K.$, O_2F_2 at $140^{o}K.$, and ClF_3 at $190^{o}K$.

It is readily soluble in anhydrous HF at $190^{o}K.$, forming a deep violet solution. The solubility is high and a 65 weight % or 23 mole % O_2ClF_3 solution is not saturated at $190^{o}K$.

This solution is not an electrolyte. A 0.5 M solution of O_2ClF_3 in HF had specific conductivity of 3.57×10^{-3} ohm^{-1} $cm.^{-1}$ at $195^{o}K.$, while the pure anhydrous HF used had the same conductivity. After decomposition the residual clear and colorless solution of ClF_3 in HF also had the conductivity of 3.57×10^{-3} ohm^{-1} $cm.^{-1}$

In contrast, a 0.5 M solution of a typical electrolyte, KF in HF, has a specific conductivity of 86.0 ohm^{-1} $cm.^{-1}$, or approximately 25,000 greater. Thus, the possibility that our violet compound might be ionic or saltlike, dissociating, for example, into ions,

$$[O_2ClF_2]^+ \text{ and } F^-$$

is excluded.

The stability of the O_2ClF_3 solution in anhydrous HF is much less than that of the pure compound. It shows a remarkable dependence on the partial pressure of O_2. At an O_2 pressure of 1.0 to 1.5 atm. and at 195°K. the concentrated solution can be kept for many hours; when the O_2 pressure is reduced to 50 to 20 mm. of Hg the deep violet solution decolorizes in a few minutes by decomposition to

$$O_2ClF_3 \xrightarrow{HF} O_2 + ClF_3 \qquad (6)$$

It is indicated that the easy decomposition is at least partly due to the formation of an intermediate complex:

$$ClF_3 + HF \rightleftarrows H[ClF_4] \qquad (7)$$

which weakens the bonds in the O_2ClF_3 molecule and promotes the liberation of O_2. Although the acidic complex itself is not known, the corresponding salts, such as $Cs[ClF_4]$ and $Rb[ClF_4]$, do exist.

A. Preparation of O_2ClF_3 by Direct Addition of Pure O_2F_2 to Pure ClF

In a typical example 1.130 grams of O_2F_2 were vacuum-distilled into a borosilicate glass reaction vessel (Kel-F test tubes may also be used) of about 100 cc. volume, melted, distributed evenly on the walls of the lower half of the reaction vessel by rotation, and frozen at 90°K. The stoichiometric amount (1:1 mole) or 0.880 gram of ClF (measured as a gas) was added in portions of $\simeq$ 100 mg. After each addition the reaction vessel was warmed up to 119°K. (melting point of ClF) and then slowly to 140°K. The violet compound, O_2ClF_3, is rapidly formed, by direct addition:

$$n\ O_2F_2 + n\ ClF \longrightarrow (O_2ClF_3)_n \qquad (4)$$

while simultaneously the white solid ClF_3 is also formed, coupled with evolution of O_2 and small and varying amounts of F_2.

The overheating can readily lead to the decomposition of O_2ClF_3, in line with equation (8):

$$O_2ClF_3 \longrightarrow O_2 + ClF_3 \qquad (8)$$

The same overheating can also lead to a simple decomposition of O_2F_2, following equation (9):

$$O_2F_2 \longrightarrow O_2 + F_2 + 4.73\ \text{Kcal.} \qquad (9)$$

The extent of each reaction can be determined by simple analysis of the gases for O_2 and F_2, since only reaction (9) leads to elementary fluorine and reaction (4) takes place without evolution of O_2 or F_2.

After each addition the reaction vessel is again cooled to 90°K., O_2 and F_2 are evacuated (and collected if desired), a fresh portion of ClF is added, and the cycle is repeated.

In this example only negligible traces of F_2 were found, while the amount of O_2 evolved equaled 205.8 cc.(N.T.P.) or 0.294 gram of O_2. Thus, all the oxygen liberated was due only to reaction (8), corresponding to 56.9 weight % of the O_2F_2 used. The rest, or 43.1 weight %, combined, following equation (4), with ClF. Thus, the yield was 43.15% of theory:

The overall material balance is:

Reagents Used	Grams	Products Formed	Grams
O_2F_2	1.130	O_2ClF_3	0.869 by calculation (see above)
ClF	0.880	O_2	0.294 by gas analysis
Total	2.010	F_2	0.000 by gas analysis
		ClF_3	0.847 by difference
		Total	2.010

After decomposition of O_2ClF_3 the total amount of ClF_3 produced in the preparation equaled 1.493 grams, as determined by direct weighing.

B. Preparation from O_2F_2 and ClF in Presence of Solvent

The yield of O_2ClF_3 can be substantially increased by carrying out the reaction in the presence of an inert solvent. With perfluoropropane, C_3F_8 (m.p. 90°K., N.B.P. 235°K.) the yield and concentration of O_2ClF_3 were increased to 81.0% of theory, as shown in the following preparation.

O_2F_2 (1.51 grams) and C_3F_8 (15.32 grams) were cooled in a borosilicate glass reaction vessel to 130°K. In a second tube the equivalent amount of ClF (1.17 grams) was dissolved in 13.58 grams of C_3F_8 (at 150°K. over 33 weight % ClF are soluble in it; at 160°K. it mixes homogeneously) and distilled into the reaction vessel. The ClF reacted immediately with the O_2F_2, forming O_2ClF_3, which being practically insoluble in C_3F_8, deposited on the walls of the reaction vessel. In all, 91.0 cc. of O_2 (N.T.P.) were evolved, accompanying the formation of ClF_3, which contaminated the O_2ClF_3 to an extent of 19.0 weight%. Unfortunately, ClF_3 is insoluble in C_3F_8; at present no method is known for separating ClF_3 from O_2ClF_3. The solvent C_3F_8 can be readily pumped off, in a vacuum, preferably at 130° to 140°K.

(Freon 13, $CClF_3$, is a solvent for O_2F_2, but in its presence the thermal stability of O_2ClF_3 is markedly decreased. With Freon 12, CCl_2F_2, as a solvent no violet compound is formed, while with ClO_3F the yield was much smaller than with pure O_2F_2 and ClF.)

C. Formation of O_2ClF_3 in Reactions of O_2F_2 with Cl_2 and HCl

O_2ClF_3 is also formed if Cl_2 is added to O_2F_2. Here, the first step is the fluorination of Cl_2 to ClF, following the equation:

$$O_2F_2 + Cl_2 \longrightarrow O_2 + ClF \tag{10}$$

After ClF is formed it reacts, as described above, to form O_2ClF_3.

HCl reacts at 130° to 140°K. with O_2F_2, in accordance with the stoichiometric equation:

$$2\ O_2F_2 + HCl \longrightarrow O_2ClF_3 + HF + O_2 \tag{11}$$

The reaction steps probably first consist in the formation of Cl_2 and then ClF, in line with the equations:

$$O_2F_2 + 2\ HCl \longrightarrow 2\ HF + O_2 + Cl_2 \tag{12}$$

and

$$O_2F_2 + Cl_2 \longrightarrow 2\ ClF + O_2 \tag{10}$$

the ClF formed reacting in the usual manner to form O_2ClF_3.

Since the above fluorination reactions of both HCl and Cl_2 are exothermic, the yields of O_2ClF_3 are lower than with ClF as described above. The activation energies, however, may be less, particularly with HCl, and thus the reaction may be initiated at lower temperatures.

At 130° to 140°K. HCl is a solid (m.p. 158.9°K.), but has a vapor pressure of $\simeq$ 10 mm. of Hg at 140°K. Thus, the reaction takes place between gaseous HCl and gaseous or liquid O_2F_2. The violet compound partly deposits on the walls, but also dissolves in liquid O_2F_2. Solutions containing up to 8.5 weight % O_2ClF_3 in O_2F_2 were obtained.

At temperatures above 140°K. the reaction proceeds rapidly, with substantial amounts of O_2ClF_3 decomposing to O_2 and ClF_3.

D. Formation of O_2ClF_3 Directly from O_2 and ClF_3 Under Influence of Ultraviolet Light

When pure liquid ClF_3 is placed in a quartz tube, and in a dry ice cavity—i.e., at a temperature of 195°K.—under a pressure of $\simeq$ 2 atm. of O_2 and irradiated with ultraviolet light, mainly at a wave length of 2537 Å., and with an intensity of 7 mw. per sq. cm., a violet compound is produced in a few seconds, probably our O_2ClF_3, in line with the equation:

$$ClF_3 + O_2 \xrightarrow[U.V.]{} O_2ClF_3 \tag{13}$$

The color of the ClF_3 solution increased appreciably with time. However, if the O_2 pressure equaled 15 mm. of Hg, no violet compound was formed. (A check experiment with pure ClF_3, in the absence of O_2, also failed to produce any violet compound).

If ozone, O_3, was used instead of O_2, in the same experiment, no violet compound formed. Some O_3 decomposed, because of the irradiation, as observed from the increase in total pressure. The addition of O_2 to the system did not cause the formation of the violet compound. Evidently the heat of decomposition of ozone is sufficient to cause the decomposition of any violet compound formed.

E. Reactions of O_2ClF_3

The violet compound is a very strong oxidizer, even at low temperatures. In this respect it is similar to the highly reactive ozone, which, for example, reacts with NH_3 even at 150°K.(14) Usually no chemical reactions take place in a temperature range of 100° to 150°K. with the exception of free radicals or atoms, as has been strikingly demonstrated by H. Broida and his associates at the National Bureau of Standards.

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(14) A. V. Grosse and A. G. Streng, Project 7-7968, Research Institute of Temple University, Technical Note No. 4, (August 1, 1957); Contract AF18(60)-1475.

A study was made of the reactions of O_2ClF_3 with NH_3, the hydrocarbons CH_4, C_2H_6, C_2H_4, and C_6H_6, H_2, and H_2O. In most cases fluorine has a preferential affinity for hydrogen and HF is usually formed.

1. Reaction with NH_3.

When gaseous NH_3 is suddenly admitted to a reaction vessel containing O_2ClF_3 at 90°K., reaction takes place with a flash, forming white solids and some nitrogen-containing gases, while the violet color disappears.

If the ammonia is condensed first in the upper part of a reaction tube cooled to 90°K., the reaction proceeds slowly as the vessel is warmed to 150° to 160°K. Ammonia has a vapor pressure of about 1 mm. at 160°K. and reacts slowly as a gas with the solid O_2ClF_3. Under these conditions the reaction proceeds smoothly without any gas evolution, while the violet color disappears and a white solid is formed. Under the same conditions pure solid ClF_3 reacts much more slowly; this is to be expected, since, in any reaction with a fuel, the components temperature range of 100° to 150°K. with the exception of free radicals or atoms, as has been strikingly demonstrated by H. Broida and his associates at the National Bureau of Standards.

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Ammonium fluoride and other ammonium salts, HF, HCl, and the oxy-acids of chlorine (either free or as ammonium salts) were identified among the reaction products.

Hydrogen fluoride was identified by vacuum distillation, formation of NaF.HF, and titration. Hydrogen chloride was identified through formation of silver chloride. Ammonia was determined quantitatively by Kjeldahl's method. The oxynitrogen acids or oxychlorine acids were identified qualitatively by Lunge's reagent. Anions of the oxychlorine acids—i.e., chlorite, chlorate, or perchlorate—were identified by reduction with zinc to chloride ion.

In one experiment 0.25 gram of O_2ClF_3 was reacted with about 0.10 gram of ammonia; 52 mg. of NH_3 was found in the reaction product together with about 3 mg. of N_2 (gas). Thus, about one half of the ammonia added formed ammonium salts. (This mixture of ammonium salts and oxidizers is potentially dangerous and can detonate!)

2. Reactions with Hydrocarbons.

With CH_4: O_2ClF_3 does not react with an excess of liquid methane at 90°K., or with gaseous methane at a pressure of 100 mm. of Hg at 150°K. During one hour there was neither a decrease in pressure nor a disappearance of the violet color.

With C_2H_6: Ethane, in contrast to methane, when admitted to the violet compound at a temperature of 140°K., reacts immediately. The violet color disappears and white solids are formed, but no gas is evolved—i.e., no formation of O_2, F_2, or CO is observed.

Hydrogen fluoride was also identified.

With $CH_2:CH_2$: The reaction vessel containing 1.39 grams of O_2ClF_3 was cooled to 120°K. and ethylene gas was introduced (ethylene has a vapor pressure of about 1.0 mm. of Hg at 120°K.) in portions of about 5 mg. at a rate of about 1 mg. per second. After an interruption of 1 to 2 minutes, new portions were added.

Under those conditions ethylene reacted immediately, causing decolorization of the violet compound and formation of the white solid products, while no measurable gas evolution—i.e., no formation of O_2, F_2, or CO—took place.

On one occasion when ethylene was added at a higher rate, the reaction proceeded with a flame which extinguished itself as soon as the ethylene flow was stopped. A total of 0.179 gram of ethylene was added to 1.3 grams of O_2ClF_3; the temperature of the bath after this addition was slowly raised at the rate of 1° to 15° per minute. No gas evolution was noticed up to 140°K. At 140°K. a violent explosion took place, shattering the reaction vessel and a large part of the reaction system. Evidently, intermediate or partly oxidized products were formed.

In all reactions of O_2ClF_3 with hydrogen-containing substances, HF is the most likely reaction product. Carbonyl fluoride, COF_2, and other intermediate oxyfluorides—for example, oxalyl fluoride, $C_2O_2F_2$—may be formed. In view of the violent explosion which took place, it is also likely that some C-H-containing compounds were present.

3. Reaction with Hydrogen.

During one hour at 90° to 120°K. there was no noticeable reaction between O_2ClF_3 and hydrogen gas at a pressure of 100 mm. of Hg. Any reaction would be characterized by disappearance or change in the violet color or decrease in the pressure of hydrogen.

The nonreactivity of O_2ClF_3 with hydrogen and methane parallels the chemical properties of ozone. Pure (100%) ozone can be mixed at -78°C. and even at room temperature with hydrogen and methane without reaction.(15,16) (The mixture 1.5 CH_4 + 2 O_3, at 804 mm. of Hg, showed at + 21°C. a pressure increase of 26 mm. of Hg on standing for 1.0 hour.)

From the present preliminary evidence it is likely that O_2ClF_3 will be more reactive than ozone at low temperatures.

4. Reaction with Benzene.

The violet compound reacts violently with a solution of benzene in HF at 195°K. A few milligrams of C_6H_6, dissolved in HF, were distilled over into a Kel-F reaction vessel containing a 1 to 2% solution of O_2ClF_3 in HF, and frozen on the walls above the O_2ClF_3 solution. The tube was then warmed up to 195°K.; the melting HF began to run down, carrying the C_6H_6. Sparks were observed when the C_6H_6 came into contact with the O_2ClF_3 solution and the violet color disappeared rapidly.

5. Reaction with Water.

To test the reactivity of O_2ClF_3 with H_2O, pulverized ice, cooled to 90°K., was added to the O_2ClF_3 contained in a tube and the tube was slowly warmed. A visible reaction started

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(15) A. G. Streng and A. V. Grosse, Advan. Chem. Ser., No. 20, 40 (1959).

(16) A. G. Streng and A. V. Grosse, J. Am. Chem. Soc., 79, 3996 (1957).

at about 130°K. with gas evolution and formation of a white solid. Oxygen was liberated and HF and $ClOH$ (or ClO_2H) were formed. The reaction proceeded much faster at higher temperatures.

Further studies of this very interesting compound, as to both its physical properties and structure and its chemical reactivity, are indicated.

V. THE CHEMICAL CHARACTERIZATION OF DIOXYGEN DIFLUORIDE

Out of four oxygen fluorides known (OF_2, O_2F_2, O_3F_2 and O_4F_2), the chemistry of dioxygen difluoride was studied most extensively. The main results obtained to date are summarized below.(17)

Dioxygen difluoride was prepared directly from the elements by the method described before.(7) It was stored in a Pyrex glass cylinder, frozen at 90°K. Chlorine monofluoride, ClF, nitryl fluoride, NO_2F, phosphorus trifluoride, at about 130°K. with gas evolution and formation of a white solid. Oxygen was liberated and HF and ClOH (or ClO_2H) were formed. The reaction proceeded much faster at higher temperatures.

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(17) A. G. Streng, "The Chemical Properties of Dioxygen Difluoride". Accepted for publication in J. Am. Chem. Soc. (1963).

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(17) A. G. Streng, "The Chemical Properties of Dioxygen Difluoride". Accepted for publication in J. Am. Chem. Soc. (1963).

PF_3, and silicon tetrafluoride, SiF_4, were also prepared by the well known methods.(18,19,20,21)

All other reagents were the commercial products of the highest available purity, supplied by Stauffer Chemical Co., General Chemical Division of Allied Chemical Co., Pennsalt Chemicals Corp., E. I. du Pont de Nemours and Co., Matheson Co., Air Reduction Co. and others. Most of these reagents were further purified by fractional distillation.

Since dioxygen difluoride is stable only at low temperatures, its chemistry was studied in a temperature region which is substantially below the usual range of chemical studies, especially because the interest lay in the energy-rich reaction products.

The experimental conditions were varied according to the requirements of each combination of reagents. In most cases, O_2F_2 was first frozen on the walls or on the Raschig-ring packing of the reaction vessel. The second reagent was then added in small portions by vacuum distillation and condensed above the O_2F_2. The vessel was then slowly warmed to the

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(18) O. Ruff, E. Ascher and F. Laas, Z. anorg. allgem. Chem., 176, 256 (1928).

(19) Georg Brauer, "Handbuch der Präparativen Anorganischen Chemie", Ferdinand Enke Verlag, Stuttgart, 1954.

(20) L. Lebouche, W. Fischer and W. Biltz, Z. anorg. allgem. Chem., 207, 64 (1932).

(21) O. Ruff and E. Ascher, Z. anorg. allgem. Chem., 196, 413 (1931).

temperature of reaction. The solid and liquid products remained in the reaction vessel, and the gaseous products were removed for analysis. The reaction vessel was then cooled again to the original temperature and a new portion of reagent was added. The procedure was repeated until all the O_2F_2 was consumed. The reaction products (gaseous, liquid and solid) were measured and analyzed.

If O_2F_2 was used as liquid, it was condensed in the bottom of the reaction vessel. In some cases reactions were performed with O_2F_2 dissolved in a suitable solvent. Two-limb apparatus was used for some of the reactions between two liquid reagents or their solutions. The reagents were condensed separately in the two limbs and one liquid was added to the other by tilting the apparatus.

If a reaction between liquid O_2F_2 (or its solution) and a gas was studied, the gas, usually diluted with an inert gas, was bubbled through the liquid.

The reagents and the reaction products were measured carefully. In the gaseous and in the liquid phase, they were measured volumetrically; in the solid phase, by weight. The reaction products were identified by chemical methods, by determination of their physical constants and by infrared spectrography.

Liquid nitrogen, liquid oxygen, various Freons and dry ice were used as refrigerants.

It must be emphasized that inadequate cooling or a fast addition of reagents to O_2F_2 and vice versa caused explosions.

A. The Reactivity of O_2F_2 with Organic Compounds

Being a high energy oxidizer, dioxygen difluoride reacts vigorously with organic compounds, even at temperatures close to its melting point. It reacted instantaneously with solid ethyl alcohol, producing a blue flame and an explosion, When a drop of liquid O_2F_2 was added to liquid methane, cooled at 90°K., a white flame was produced instantaneously, which turned green upon further burning. When 0.2 cm^3 of liquid O_2F_2 was added to 0.5 cm^3 of liquid CH_4 at 90°K., a violent explosion occurred.(22)

When added to dry ice, dioxygen difluoride does not react and is only absorbed by the solid. Addition of acetone to this mixture resulted in sparking accompanied by an explosion.

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(22) A. D. Kirshenbaum, J. G. Aston and A. V. Grosse, Final Report, Contract No. DA-36-034-ORD-2250, Research Institute of Temple University, Philadelphia 44, Pa., November 18, 1958.

A 2% solution of O_2F_2 in HF reacts violently with a flash with benzene at 195°K.(12)

B. Reactivity with Ammonia, Water and Hydrogen

Liquid dioxygen difluoride reacts vigorously when added to solid anhydrous ammonia at temperatures close to 110°K. It causes explosions when added to ice at 130-140°K. and reacts also with traces of water if dissolved in HF containing H_2O, at 195°K., the brown color of the solution disappears and the O_2 gas escapes.

In view of the high reactivity of hydrogen atoms at low temperatures, it was considered of interest to study their reaction with O_2F_2. It was hoped that since they are likely to abstract fluorine, forming HF, intermediate species, either radicals or others, may be formed under suitable conditions. The H-atom generator used was described elsewhere.(12)

Dioxygen difluoride was condensed in the form of a ring on the walls of a U-tube cooled to 77°K. There was no reaction between O_2F_2 and molecular hydrogen when gas was pumped through to the U-tube at 77°K., in amounts of 1.25 lit./hr., P = 1 mm. Hg. Atomic hydrogen, however, reacted with O_2F_2 at the same conditions, forming a white solid. Several times during the experiment, the H-atom generator was turned off, O_2F_2 warmed up to its melting point and allowed to separate from the layer of reaction products, which covered the O_2F_2 and prevented its further reaction. After about 2/3 of the O_2F_2 was consumed, the generator was turned off, the U-tube warmed to the melting point of O_2F_2 and the excess of O_2F_2 pumped off.

The investigation of the reaction products showed that the reaction proceeded in accordance with the equation:

$$3\ O_2F_2 + 15\ H\cdot \longrightarrow 6\ HF + 1.5\ H_2O_2 + 3\ H_2O. \quad (14)$$

Traces of H_2O_4 were also formed. No radical or other intermediate products have been found.

C. Reaction with Cl_2, ClF and HCl

A rapid introduction of chlorine to dioxygen difluoride, cooled to about 140°K., causes a violent explosion. However, when small portions of Cl_2 are added slowly to O_2F_2 cooled to 130°K., a violet intermediate product does form, together with ClF_3.(13) here, the first step is the fluorination of Cl_2 to ClF:

$$O_2F_2 + Cl_2 \longrightarrow O_2 + 2\ ClF \qquad (10)$$

After ClF is formed, it reacts further with O_2F_2 as described below.

The study of the reaction of O_2F_2 with ClF showed that if the reaction is carried out without special precautions at temperatures above 140°K., the two substances react violently with heat evolution following the stoichiometric equation:

$$O_2F_2 + ClF \longrightarrow O_2 + ClF_3 + 30.1\ Kcal \qquad (15)$$

The ClF abstracts the fluorine from O_2F_2, forming ClF_3 and liberating O_2. Simultaneously, due to the heat of reaction (15), a part of O_2F_2 decomposes to O_2 and F_2. However, if the reaction between O_2F_2 and ClF is carried out at moderate temperatures (119-130°K.) and with a slow addition of ClF, a third reaction, besides the reaction (15) and (9) takes place, forming an intermediate compound of the elementary composition $(O_2ClF_3)_n$ in accordance with the equation (4). The extent of each of the reactions depends upon the reaction conditions.

The intermediate compound, dioxygen chlorine trifluoride has an intense violet color and is a very strong oxidizer. Its properties are described in section IV of this Report.

Dioxygen chlorine trifluoride, O_2ClF_3, was formed also in the reaction of O_2F_2 with HCl at 130-140°K. The analysis of the reaction products showed that the reaction proceeds in accordance with the equation:

$$2\ O_2F_2 + HCl \longrightarrow O_2ClF_3 + HF + O_2 \qquad (11)$$

As an example, 65.0 mg. of O_2F_2 was reacted with 17.0 mg. of HCl. The oxygen evolved was determined by absorption in an alkaline pyrogallol solution. The hydrogen fluoride formed was combined with NaF and determined by titration with 1/10 N NaOH after decomposing the violet compound and distilling off the ClF_3. The additional O_2 evolved upon decomposition of O_2ClF_3 was determined separately. The chlorine trifluoride was measured as a gas and identified by the infrared spectrum. The yield of O_2ClF_3, calculated from the amount of O_2 evolved upon decomposition of the violet compound, was about 41%. The material balance of the reaction is presented in Table II.

The suggested reaction steps are as follows:

$$\begin{array}{lr}
O_2F_2 + 2\ HCl \longrightarrow 2HF + O_2 + Cl_2 & (12) \\
O_2F_2 + Cl_2 \longrightarrow 2\ ClF + O_2 & (10) \\
\underline{2\ O_2F_2 + 2\ ClF \longrightarrow 2\ O_2ClF_3} & (\ 4) \\
4\ O_2F_2 + 2\ HCl \longrightarrow 2\ O_2ClF_3 + 2\ HF + 2\ O_2 & (11)
\end{array}$$

An excess of HCl and a rise of temperature above 140°K. caused fast decomposition of O_2ClF_3.

TABLE II

Material Balance of an O_2F_2 + HCl Experiment

Reaction Products Found		Reaction Products Expected
O_2 evolved during the reaction	12.0 cm^3 or 17.2mg.	-----
O_2 evolved upon decomposition of violet compound	8.5 cm^3 or 12.1 mg.	-----
O_2 total	20.5 cm^3 or 29.3 mg.	10.5 + 10.2 = 20.7 cm^3 or 29.6 mg.
HF	9.4 mg.	9.5 mg.
ClF_3 total	11.0 cm^3 or 45.4 mg.	10.4 cm^3 or 42.9 mg.
TOTAL	84.1 mg.	82.0 mg.

At 130 and 140°K., HCl is solid (m.p. 158.9°K.) but it has a vapor pressure of about 10 mm. Hg at 140°K. Thus, the reaction actually takes place between gaseous HCl and gaseous or liquid O_2F_2. The violet compound partly deposited on the walls, but also dissolved in the liquid O_2F_2. Solutions containing up to 8.5% by weight of O_2ClF_3 in O_2F_2 were obtained.

Finally, the violet product formed also when pure liquid ClF_3 in a quartz tube under pressure of $\simeq$ 2 atm. O_2 was irradiated with ultraviolet light at 195°K. However, if the O_2 pressure is only 15 mm. Hg or O_3 is used instead of O_2, the violet product does not form.

No reaction was observed between O_2F_2 and ClF_3 in the solid state at 90°K., or in the liquid state at temperatures up to 190°K.

D. Reaction with Br_2, Bromine Fluorides and HBr

Liquid O_2F_2, at temperatures close to its melting point (109.7°K.), reacted vigorously when added to solid bromine cooled to 90°K.

When liquid BrF_3 cooled to its melting point (282°K.) was dropped onto solid O_2F_2 cooled to 90°K., a spontaneous reaction occurred with evolution of heat and gas. Analysis of the reaction product showed that the reaction proceeded in accordance with the equation:

$$O_2F_2 + BrF_3 \longrightarrow BrF_5 + O_2 + 46.1 \text{ Kcal} \qquad (16)$$

The O_2 was identified by the usual method of gas analysis and the bromine pentafluoride by determination of its melting point (= 211.9°K.), boiling point (= 313.7°K.) and density (= 3.09 g/cm^3 at 212°K.).

Under milder conditions, in some experiments a brown-violet intermediate product was obtained. The formation of this product was, however, not always reproducible for unknown reasons. In these experiments, BrF_3 was condensed on the walls of the reaction vessel at 90°K. A thin layer of O_2F_2 was then condensed on the BrF_3. The bath temperature was raised slowly and at about 130°K. the reaction between BrF_3 and O_2F_2 began, forming a violet-brown compound, with some gas evolution. Analysis showed that the gas consisted mainly of oxygen (with a small amount of fluorine). The colorless liquid reaction product was identified as BrF_5. The small amount of F_2 was due to the partial decomposition of O_2F_2. An example of a weight balance of reagents and products is given in Table III. In this experiment a 73 wt.% yield of the violet-brown O_2BrF_5 was obtained.

The violet-brown compound began to decompose at 150°K. and decomposed completely at 170°K. to oxygen and BrF_5.

The formation of the colored intermediate product proceeded analogously to the O_2F_2 + ClF reaction, in accordance with the equation:

$$O_2F_2 + BrF_3 \longrightarrow O_2BrF_5 \tag{17}$$

TABLE III

Material Balance of the $BrF_3 + O_2F_2$ Experiment

Reagents used: 884 mg. BrF_3 + 452 mg. O_2F_2; $\Sigma = 1336$ mg.

980 mg. O_2BrF_5 was formed; yield ≃ 73 wt.%.

Reaction Products Obtained		Reaction Products Expected after complete decomposition
O_2 evolved during the reaction		
27.0 cm^3, or 38.6 mg.		------
O_2 evolved upon decomposition of the intermediate colored product		
106.0 cm^3, or 151.5 mg.		------
O_2 total		
133.0 cm^3, or 190.1 mg.		144.6 cm^3, or 206.6 mg.
BrF_5 total		
0.37 cm^3 at m.p., or 1143 mg. of liquid		1129.4 mg.
F_2 total		
traces		------
TOTAL	1333.1 mg.	1336.0 mg.

This reaction was always accompanied by some gas evolution due to decomposition of O_2BrF_5 to BrF_5 and O_2 and to partial decomposition of O_2F_2 to O_2 and F_2.

Reaction (17) is more difficult to control than reaction (4).

At approximately the same conditions, dioxygen difluoride reacted with a mixture of Br_2, BrF and BrF_3. Ruff and Menzel(23) and Braida(24) reported that upon mixing Br_2 and BrF_3, an intermediate species, BrF, is formed. However, pure BrF was not isolated as yet, owing to its dissociation into Br_2 and BrF_3. Fischer and coworkers(25,26,27) found that in the gas phase the reaction:

$$Br_2 + BrF_3 \longrightarrow 3\ BrF \qquad (18)$$

took place to varying extent.

In the experiments with O_2F_2, a product obtained by mixing BrF_3 with 10% of Br_2 was used. This product reacted with O_2F_2 between 90° and 130°K., forming a dark-brown (violet shaded) intermediate, which decomposed to BrF_3 and BrF_5 at temperatures above 130°K. If the reaction was carried out at temperatures above 130°K., it proceeded rapidly and directly to BrF_3, BrF_5 and O_2, without forming any colored intermediates.

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(23) O. Ruff and W. Menzel, Z. anorg. u. allgem. Chem., 202, 60 (1931).

(24) O. Ruff and A. Braida, Z. anorg. u. allgem. Chem., 214, 87 (1933).

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The colored intermediate products formed with BrF_3 and Br-BrF-BrF_3 mixture have only a transitory existence and attempts to stabilize them were not successful. Moreover, these reactions are not always reproducible.

The study of the reaction between O_2F_2 and HBr showed that when a small amount of O_2F_2 reacts with an excess of HBr at about 130°K. the reaction proceeds according to the equation:

$$O_2F_2 + 2\ HBr \longrightarrow 2\ HF + Br_2 + O_2 \qquad (19)$$

Dioxygen difluoride was condensed on Raschig-rings in the reaction vessel. HBr was added at 90°K., allowed to condense above the O_2F_2 and the vessel was then slowly warmed to 130°K. Dioxygen difluoride melted and its vapor reacted with the excess of HBr, liberating Br_2 and O_2. The free bromine, when warmed to 140°K., reacted with O_2F_2 forming colorless BrF_5. No additional colored products were formed. When, however, the HBr layer was condensed lower and contacted with an excess of liquid O_2F_2 at 130°K., a violet compound similar in appearance to O_2BrF_5, formed. The measurements and the analysis of the reaction products indicated that with an excess of O_2F_2, the reaction most probably proceeds in accordance with the equation:

$$3\ O_2F_2 + HBr \longrightarrow O_2BrF_5 + HF + O_2 \qquad (20)$$

The colored intermediate product decomposed at higher temperatures, forming BrF_5 and liberating gaseous O_2.

E. Reactivity with I_2 and IF_5

A spontaneous reaction occurred when liquid O_2F_2 cooled to about 110°K. was added rapidly to iodine crystals cooled to 90°K. There was no visible reaction between 8-50% solutions of O_2F_2 in Freon 13 ($CClF_3$) and iodine at temperatures up to 195°K.

Iodine pentafluoride, IF_5, in contrast to its chlorine and bromine analogs (ClF and BrF_3), did not react with O_2F_2 over the temperature range of 90-195°K. Only a slow decomposition of O_2F_2 to O_2 and F_2 took place. Under more drastic conditions the formation of iodine heptafluoride, IF_7, will probably take place.

F. Reaction with Phosphorus and PF_3

With red phosphorus, O_2F_2 reacted vigorously when added rapidly at about 110°K.

Phosphorus trifluoride, PF_3, reacted with O_2F_2 at 125°K. forming PF_5 and O_2:

$$O_2F_2 + PF_3 \longrightarrow PF_5 + O_2 \qquad (21)$$

At the same time some of the liberated oxygen reacted with PF_3, forming a white solid whichwas fairly stable at 0°C. This compound was the only solid reaction product; it was not the well known POF_3, which melts at 233.4°K. and boils at 233.8°K., but rather an interesting polymer of POF_3:

$$n\ O_2F_2 + 3nPF_3 \longrightarrow nPF_5 + 2(POF_3)_n \qquad (22)$$

On standing at 0°C. or at room temperature, the polymer depolymerized completely to POF_3:

$$(POF_3)_n \longrightarrow n(POF_3). \qquad (23)$$

If the amount of PF_3 added in one portion was larger than 50 mg. or if the compounds were warmed quickly, the reaction proceeded with flame.

G. Reactivity with NO_2F, NF_3 and N_2F_4

Dioxygen difluoride is soluble in nitryl fluoride, NO_2F, at 195°K., forming a very fluid orange solution. A slow decomposition of O_2F_2 takes place at this temperature, but no reaction with NO_2F was observed.

There was no visible reaction between nitrogen trifluoride, NF_3, and O_2F_2 at 130°-140°K. Tetrafluorohydrazine,

N_2F_4, reacted with O_2F_2 at 170°K., forming NF_3 and O_2, but without the formation of any colored intermediate product.

Our experience with N_2F_4 showed that upon distillation, either in Pyrex glass or in a Kel-F system, the tetrafluorohydrazine itself (or an impurity or a reaction product with glass) forms a dark violet compound, which looks like the violet compound formed by the reaction between O_2F_2 and ClF. It was made clear, however (before using N_2F_4 for the reaction with O_2F_2), that this voilet compound is not of the same type as that obtained in the O_2F_2 + ClF reaction. The violet compound formed by N_2F_4 could be distilled, for example, from one vessel into another, together with N_2F_4 without decomposition, whereas O_2ClF_3 is nonvolatile.

According to Johnson and Colburn,(28) condensation of cold gaseous N_2F_4 (-30°C.) at relatively high pressures, gives a water-white liquid. However, if the gas is condensed at elevated temperatures and low pressures, the liquid obtained has a color varying from light blue to blue-black. The color is said to be due to trace amounts of nitrosodifluoramine, NF_2NO.(29)

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H. Reaction with S, SF_4 and H_2S

When added rapidly to sulfur cooled to 90°K., liquid O_2F_2 reacted instantaneously with a flash.

Sulfur tetrafluoride, SF_4, reacted violently with concentrated O_2F_2 at about 130°K., forming SF_6 and O_2:

$$O_2F_2 + SF_4 \longrightarrow SF_6 + O_2 + 121.5 \text{ Kcal.} \qquad (24)$$

The solutions were used, therefore, to prevent too violent reactions. Sulfur tetrafluoride diluted with ClO_3F (2:3 by volume) was distilled into the reaction tube containing frozen O_2F_2 at 90°K. Traces of an intermediate violet-purple compound formed immediately on the walls of the reaction vessel, even at 90°K. Most of the SF_4 and ClO_3F condensed on the walls above the O_2F_2. The tube was then warmed above 125°K. At about 130°K. the SF_4-ClO_3F mixture began to melt and flow down to the O_2F_2. More purple-violet compound formed and the reaction went out of control with an explosively violent evolution of gas and heat. The excess of unreacted O_2F_2 remained on the bottom of the shattered reaction tube. The reaction between highly diluted O_2F_2 and SF_4 proceeds without violence, but the intermediate colored product either forms in very small amounts or does not form at all.

A 12.8% by weight O_2F_2 solution was used, for example. It was frozen at 90°K. and a gaseous SF_4-ClO_3F mixture (1:1) was added in small portions, each containing 20-100 mg. of SF_4. After the addition of each portion, the reaction vessel was warmed to 130°K. Only traces of violet compound formed, which deposited on the walls of the reaction vessel above the O_2F_2-ClO_3F mixture. The formation of the violet compound took place only at temperatures of 90°-116°K. At 130°K. a slow visible reaction between O_2F_2 and SF_4 began, with evolution of O_2 gas and formation of SF_6. Further warming to 150°-170°K. increased the reaction rate and caused decomposition of the colored compound. Also, decomposition of O_2F_2 to O_2 and F_2 was noted.

The use of a smaller amount of diluent gave a larger quantity of the colored intermediate product, but it could not be preserved. The formation of the colored intermediate product probably proceeds similarly to the formation of the colored products in the O_2F_2 + ClF and O_2F_2 + BrF_3 reactions:

$$O_2F_2 + SF_4 \longrightarrow O_2SF_6 \qquad (25)$$

This reaction is even more difficult to control than reaction (17). In most cases it proceeds directly to the formation of SF_6 and O_2 in line with equation (24) and leads to an explosion. With perchloryl fluoride, ClO_3F as a solvent, explosions could be avoided in some cases (at temperatures below 116°K.), but the yield and the stability of the intermediate product were very low.

With H_2S, dioxygen difluoride reacted in accord with the equation:

$$4\ O_2F_2 + H_2S \longrightarrow 2\ HF + 4\ O_2 + SF_6 + 432.9\ \text{Kcal.} \qquad (26)$$

The formation of all these reaction products was established analytically. It was observed that a very slow reaction starts in the gas phase at 130°K. The vapor pressure of O_2F_2 at this temperature is about 1 mm. and of H_2S, about 0.5 mm. Hg. When the reaction vessel was further warmed slowly to 195°K., the rate of the reaction increased. In contra distinction to the O_2F_2 + HCl and O_2F_2 + HBr reactions, the $O_2F_2 + H_2S$ reaction gave no colored intermediate compound.

I. Behavior of O_2F_2 with Some Other Substances

Liquid dioxygen difluoride at temperatures close to its melting point, reacted vigorously when added to charcoal cooled to 90°K. It did not appear to react, however, with beryllium powder, quartz fiber and chromium trioxide, even upon warming to room temperature.

Solid SiF_4 (m.p. 183°K.) did not react with liquid O_2F_2. Approximately 20% of SiF_4 is soluble in liquid O_2F_2 at 150°K. without noticeable reaction. At about 195°K., O_2F_2 decomposed into O_2 and F_2, while SiF_4 remained unchanged. Similarly, CF_4 did not react with O_2F_2.

J. Thermochemistry of the Investigated Reactions of O_2F_2

The reactions of O_2F_2 with the lower fluorides of chlorine, bromine and sulfur and with HCl, HBr and H_2S tend naturally to proceed to the end, i.e., to form the most stable reaction products. In some reactions intermediate products of high oxidizing power have been obtained. This was achieved by carrying out the reactions slowly at low temperatures. It was found that the reactions of ClF and HCl with O_2F_2 are comparatively easy to control at cryogenic conditions and adequate yields of the intermediate product, O_2ClF_3, have been obtained. The reactions with bromine compounds are more difficult to control and their intermediate product, O_2BrF_5, is much less stable. Still more difficult to control are the reactions with sulfur compounds so that in most cases the analogous intermediate product O_2SF_6 does not form at all. These facts are in the logical agreement with the amounts of energy evolved. The more energy liberated the more difficult it is to quench the reaction and to freeze and stabilize the intermediate reaction product. The heats of formation, i.e., ΔH_{298}, of the compounds involved are given in Table IV.

The overall reactions which take place and the amounts of heat evolved, or ΔH_{298}, are as follows:

a. with the fluorides:

$O_2F_2 + ClF \rightarrow ClF_3 + O_2$ (15); $\Delta H_{298} = -30.1$ Kcal/formula wt

$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2$ (16); $\Delta H_{298} = -46.1$

$2\ O_2F_2 + BrF \rightarrow BrF_5 + O_2$ (27); $\Delta H_{298} = -95.7$

$O_2F_2 + SF_4 \rightarrow SF_6 + O_2$ (24); $\Delta H_{298} = -121.5$

b. with the hydrides:

$2\ O_2F_2 + HCl \rightarrow ClF_3 + HF + 2\ O_2$ (28); $\Delta H_{298} = -91.5$

$3\ O_2F_2 + HBr \rightarrow BrF_5 + HF + 2\ O_2$ (29); $\Delta H_{298} = -176.9$

$4\ O_2F_2 + H_2S \rightarrow SF_6 + 2\ HF + 4\ O_2$ (26); $\Delta H_{298} = -432.9$

It can be easily seen (see under a.) that the reaction with ClF evolves the least amount of heat and is therefore the easiest to control. This is followed by the reactions with BrF_3 and BrF. The reaction with SF_4 evolves 3 times more heat than with ClF and has been found to be the most difficult to control.

TABLE IV

Compound	ΔH_{298} Kcal/mole	Reference
	FLUORIDES	
O_2F_2	+ 4.73 ± 0.3	30
ClF	- 13.510 ± 0.11	31
ClF_3	- 38.869 ± 1.0	31
BrF	- 20	33
BrF_3	- 64.8	34
BrF_5	- 106.2	34
SF_4	- 171.7 ± 2.5	32
SF_6	- 288.5 ± 0.7	31
	HYDRIDES	
H_2S	- 4.815	31
HBr	- 8.66 ± 0.05	31
HCl	- 21.97 ± 0.09	31
HF	- 65.14 ± 0.03	31

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In making comparisons with the hydrides (see under b.) one sees that the heat evolutions follow the same sequence, i.e., HCl HBr and HBr H_2S, but that the actual values are much higher. It should not be forgotten that there are values for the overall reactions.

Actually, the hydrides react in steps, first forming HF and a fluoride. Thus,

$$O_2F_2 + HCl \longrightarrow HF + ClF + O_2 \ (30); \ \Delta H_{298} = -61.4 \text{ Kcal}$$

After this step the second step, as given under a., takes place.

VI. EXPLORATORY EXPERIMENTS

The exploratory study of the behavior and reactivity of oxygen fluorides with various substances was continued in order to obtain information on the basic chemistry of oxygen fluorides and their ability to form addition products.

A. Reaction of O_2F_2 with N_2F_2

The preliminary experiments indicate that up to 155°K. no reaction takes place between O_2F_2 and N_2F_2. When the temperature is raised to 160-170°K. some reaction occurs as evidenced by the disappearance of the red color of O_2F_2. An infrared analysis of the product showed mostly N_2F_2 and no N_2F_4 or NF_3. Besides $\simeq$ 4% SiF_4, however, small unknown peaks at 13.4 and 13.6 microns appeared in the infrared spectrum. This reaction will be studied further.

B. Reactivity of OF_2 with HCl and H_2S

At low temperatures, oxygen difluoride behaves chemically significantly different than dioxygen difluoride. With HCl and H_2S dioxygen difluoride forms highly colored intermediate products. Quite different results were obtained with OF_2.

1. With HCl

No visible reaction took place between solid HCl and liquid (or gaseous) OF_2 at 90 to 140°K. There was also no noticeable reaction between a 1:1 molar mixture of HCl and OF_2 at 25°C. and 1 atm. total pressure.

2. With H_2S

No visible reaction took place between solid H_2S and liquid and gaseous OF_2 at temperatures of 90-150°K. A 1:1 gaseous mixture, at 195°K. and 400 mm. total pressure reacted slowly forming a white solid (at 195°K.). During one hour the pressure decreased to about 100 mm. Hg. When the tube was taken out of dry ice, an explosion occurred shattering the reaction vessel.

C. Reactions of OF_2 and O_3F_2 with Atomic Hydrogen

In view of the high reactivity of hydrogen atoms at low temperatures generally it was considered of interest to study their reaction with the oxygen fluorides. It is hoped that since they are likely to abstract fluorine, forming HF, intermediate species, either radicals or others, may be formed under suitable conditions.

The H-atoms generator used was described in our First Annual Progress Report, January 3, 1961 (p. 36). The oxygen difluoride used in these experiments was obtained from Baton Rouge Development Laboratory, Allied Chemical Corp. Originally it contained 97.7 wt.T OF_2, 1.75% O_2 and 0.55% CO_2 and was purified by fractional distillation. O_3F_2 was prepared in our laboratories.

1. Experiments with OF_2

In the first variant of our experiments, a stream of gaseous OF_2, 500 $cm.^3$/hr., was passed through a U-tube cooled in a liquid nitrogen bath. Simultaneously, a stream of H_2, also 500 $cm.^3$/hr., was let through the H-atoms generator into the same U-tube. The total gas pressure in the discharge = 0.4-0.8 mm. Hg.

H-atoms reacted with OF_2 forming a white solid deposit on the walls.

In the second variant, OF_2 was condensed on the bottom of the U-tube cooled to 77°K., forming a layer of a slightly yellow liquid. The vapor pressure of OF_2 at this temperature is $\simeq$ 0.75 mm. Hg. The H-atoms were generated in a stream of H_2 gas passed through the generator with a velocity of 1.25 lit./hr. The total pressure of gas in the reaction tube $\simeq$ 1.0 mm. Hg. OF_2 reacted with H-atoms and formed a white solid deposit on the walls of the U-tube.

A stream of molecular hydrogen under the same conditions does not react with OF_2. Even at room temperature molecular hydrogen did not react with OF_2 at a total pressure of up to 1 atm.

The qualitative analysis of product obtained showed that it consisted of HF, H_2O, H_2O_2 and of a comparatively small amount of H_2O_4.

2. Experiments with O_3F_2

Liquid O_3F_2 was pipetted into the reaction tube at 90°K. in amounts of 1.0-1.7 g. and kept liquid (supercooled) at 77°K. From time to time, when the O_3F_2 solidified, it was warmed up to 90°K. and cooled again to 77°K.

There was no noticeable reaction between O_3F_2 and molecular hydrogen when the last was pumped through the reaction tube at 77°K. in amounts of about 1.25 lit./hr., P = 1 mm. Hg. But when the H-atoms generator was turned on and the H-atoms were pumped through the reaction tube, they reacted with O_3F_2 forming a white solid. There was no O_3 or any other colored reaction product formation, as well as no H_2O_4 formed. Only HF, H_2O and H_2O_2 were found in the reaction product.

In all these experiments H_2O_2 was identified by the color reaction with $Ti(SO_4)_2$. For quantitative determination it was titrated with standard $KMnO_4$ solution. Hydrogen fluoride was combined, with NaF and titrated with standard NaOH solution. H_2O_4 was identified by the evolution of O_2 gas at about 160°K.

The experiments showed that at 77°K. the reaction between H-atoms and oxygen fluorides proceeds without the formation of any colored new compounds. Probably much lower temperatures are required to obtain higher oxygen fluorides, such as O_4F_2 or O_5F_2.

D. Formation of a Blue Compound and the Reaction between O_3F_2 and ClF

In the exploratory experiments reported in our First Annual Progress Report, January 3, 1961 (p. 17) no reaction between O_3F_2 and ClF was noticed at 77 and 90°K. Observations covered however periods of a few hours only.

1. At 77°K., the reaction between the solid O_3F_2 and solid ClF proceeds so slowly that the definite formation of colored reaction products was noticed only after 5 days. At the points of contact of reagents, violet and blue compounds formed. Their amount increased with the time. The compounds have not been analyzed yet, but the violet compound is most probably our O_2ClF_3. The blue compound is new. In our Second Annual Progress Report, January 19, 1962, (p. 10) we reported already the formation of a greenish-blue compound when the violet O_2ClF_3 is warmed up to about 140°K. in the presence of ClF and ClF_3 and the formation of a blue compound while pumping off the oxygen from a violet solution of O_2ClF_3 in anhydrous HF at 190-195°K. In both cases this blue compound (or compounds) existed only for a very short time, i.e., for about 1-5 minutes. The blue compound obtained in the slow reaction between solid O_3F_2 and ClF was kept at 77°K. for 25 days without noticeable decomposition. Since ozone, O_3, could be readily formed from O_3F_2 by abstraction of fluorine it was demonstrated first that our new blue compound is not ozone. This was accomplished by extracting our reaction product with liquid O_2 at 77°K., our new blue compound is insoluble in liquid O_2, while ozone is readily soluble under the same conditions.

2. The reaction between O_3F_2 and ClF dissolved in liquid oxygen at 77°K. proceeds even slower. Only 0.05 wt.% O_3F_2 is soluble in liquid oxygen at 77°K. and the formation of our violet compound was noticed only after 10 days.

3. At 90°K. when solid ClF, condensed on the walls of a reaction vessel, is soaked with liquid O_3F_2, the formation of our violet compound (or compounds) was observed after 2-3 hours.

4. A spontaneous reaction with sparks and evolution of gas was observed when liquid O_3F_2 was dropped into an open tube containing solid ClF cooled in a liquid oxygen bath.

E. Experiments at Low Temperatures for Extended Reaction Times

In the previous investigations all the reactions were carried out for only a few hours at temperatures of up to 130-140°K. Since the ΔH's of most of the expected reactions are high, much could be gained if the reactions were carried out at lower temperatures over a period of days or weeks instead of a few hours.

A series of such reactions has been started. It was found that O_3F_2 and O_2F_2 react with ClF even at 77°K., although the reaction proceeds very slowly. The formation of the violet compound was noticed only after 3 days at 90°K., in an experiment with O_2F_2 and ClF and with liquid OF_2 as a solvent for ClF; and after 5 or even 10 days at 77°K., in an experiment with O_3F_2 and ClF in the presence of liquid oxygen. The amounts of the colored intermediates seem to increase with time. These experiments are not yet finished.

A further investigation of these reactions and of the reactions of O_2F_2 and O_3F_2 with BrF_3, HBr, SF_4, H_2S and other reagents at 77 and 90°K. for long periods of time is planned.